Articles

In Situ XPS Studies of the Deposition of TiN$_x$C$_y$ Films from Tetrakis(dimethylamido)titanium(IV) and Bis[*N*,*N*-bis(*tert*-butyl)ethylenediamido]titanium(IV)

G. Ruhl, R. Rehmet, M. Knižová, R. Merica, and S. Vepřek*

Institute for Chemistry of Inorganic Materials, Technical University Munich, Lichtenbergstr. 4, D-85747 Garching/Munich, Germany
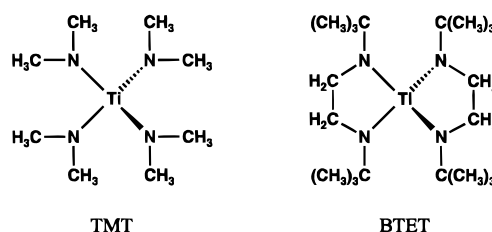
The decreasing feature size of integrated circuits requires new low-temperature, chlorine-free CVD processes for titanium nitride (TiN) diffusion barriers. The thermal deposition of TiN from organometallic precursors, e.g., tetrakis(dimethylamido)titanium (TMT), results in a high carbon contamination of the films. Using in situ X-ray photoelectron spectroscopy (XPS), we show that the contamination of TiN films deposited on silicon consists mostly of hydrocarbon inclusions and a smaller amount of titanium carbide (TiC). From these results we confirm and extend the mechanism for the thermolysis reaction of TMT proposed by other authors, showing the formation of TiC as being inherent to this precursor. The reaction of TMT with ammonia decreases the amount of carbon contamination, yet the spontaneous reaction in the gas phase results in a poor step coverage. On the basis of these results, we suggest in agreement with other authors that at small NH$_3$/TMT ratios and very low pressures the reaction proceeds via a polymeric transamination at the substrate surface. The importance of gas-phase reaction increases at higher NH$_3$/TMT ratios. Activated hydrogen from a plasma afterglow source significantly reduces the hydrocarbon contamination leaving only a small amount of hydrocarbon and carbidic carbon in the films. It is shown that at least a part of the aliphatic carbon found in the films originates from the adsorption and subsequent decomposition of the product amines at the TiN surface. Attempts to avoid the TiC formation were made by using the precursor bis[*N*,*N*-bis(*tert*-butyl)-ethylenediamido]titanium (BTET).

Introduction

Aluminum, which is currently used for the metalization in integrated circuits, alloys with silicon above about 350 °C, leading to the failure of the device. Therefore, a diffusion barrier consisting of about 100 nm thick titanium and titanium nitride sandwich interlayer is applied between the silicon and aluminum. The current technology uses reactive sputtering for TiN deposition. This technique, however, suffers from poor step coverage at high aspect ratios which are used in the recent and future submicron devices. Therefore, alternative techniques, such as low-temperature chemical vapor deposition (CVD) are being developed in order to replace the sputtering.

The conventional CVD of TiN uses the reduction of TiCl$_4$ with hydrogen in the presence of ammonia and/or nitrogen at 500–1000 °C. Future technology which is compatible with the multilevel metalization requires process temperatures not exceeding 450 °C. Even with ammonia, the TiN deposition rates achieved from TiCl$_4$ are too low and the chlorine content in the films is high. Therefore, organometallic (OM) CVD of TiN which provides a good step coverage, high deposition rate, good

Figure 1. Molecular structures of TMT and BTET.

electrical conductivity, and diffusion barrier properties is under investigation in many laboratories.

First experiments with organometallic CVD of titanium nitride from tetrakis(dimethylamido)titanium (TMT, Figure 1) were reported by Sugiyama et al. in 1975.[1] The above-mentioned need for a new process led to intense studies in recent years (e.g. refs. 2–18). TMT is a convenient precursor, because of its simple synthesis

* Author to whom correspondence should be addressed

(1) Sugiyama, K.; Pac, S.; Takahashi, Y.; Motojima, S. *J. Electrochem. Soc.* **1975**, *122*, 1545.
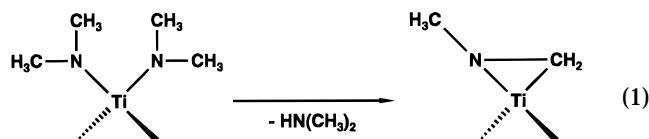(2) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Mater. Res. Soc. Symp. Proc.* **1990**, *168*, 357.
(3) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1990**, *2*, 235.
(4) Fix, R. M.; Gordon, R. G.; Hoffman, D. M. *Chem. Mater.* **1991**, *3*, 1138.
(5) Ishihara, K.; Yamazaki, K.; Hamada, H.; Kamisako, K.; Tarui, Y. *Jpn. J. Appl. Phys.* **1990**, *29*, 2103.
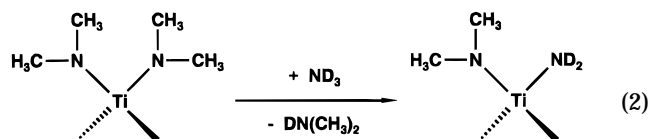
and a relatively high vapor pressure of 0.5–8 mbar at temperatures of 45–90 °C, respectively.[11] The thermal CVD from TMT provides titanium nitride films with a high carbon content (mostly CH$_x$)[3,5,6,9] and a high specific resistivity of 5×10^{-3}–1×10^{-2} Ω cm.

The reason for the high carbon content is inherent to the mechanism of the gas-phase thermolysis. The first step is the elimination of β-hydrogen from the neighboring methyl groups followed by the elimination of dimethylamine and the formation of a Ti-C-N-metallacycle (eq 1). This metallacycle leads to carbidic bonded car-
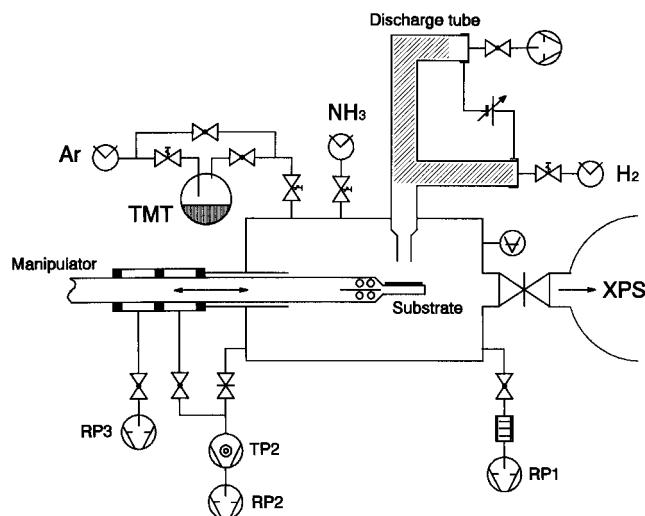

$$\text{(1)}$$

bon.[3,8,12] It will be shown that a similar reaction takes place also in surface-controlled regime at very low pressure. In addition, the gaseous reaction products dimethylamines decompose readily at the TiN surface which results in a further incorporation of non-carbidic carbon.[19]

Ammonia attacks the titanium center with its lone electron pair in a gas-phase reaction already at room temperature. This leads to the elimination of dimethylamine and the formation of amino groups. Experiments with deuterated ammonia confirmed the transamination mechanism (eq 2).[8,13] Addition of dimeth-

$$\text{(2)}$$

ylammine to the TMT/NH$_3$ gas mixture inhibits the reaction between TMT and NH$_3$, indicating that the transammination reaction should be reversible.[15] The reaction with ammonia can reduce the carbon content to a few atom percent, which leads to a significant lower resistivity of the films.[4,7] However, the spontaneous and fast reaction in the gas phase results in a poor step coverage of structured wafers.[10] Therefore, it is necessary to use very low pressure OM CVD where the reaction occurs at the surface.[18]

Figure 2. Schematic diagram of the experimental UHV system used for low-pressure OMCVD and in situ analysis by XPS

In this work we have studied the thermal decomposition and the reaction of TMT with ammonia at very low pressure, which should reduce the spontaneous gas-phase transamination and lead to the elimination of dimethylamine in the adsorbed surface layer. The results both confirm and extend the reaction mechanism of the thermolysis of TMT in eq 1 and show that the problems associated with the hydrocarbon and TiC incorporation occur also under very low pressure conditions at the surface of Si wafer. During processing this paper for the publication similar results were published by Truong et al.[18]

A possible solution of the hydrocarbon problem is found in using atomic hydrogen in the afterglow of a glow discharge as a coreactant. A part of these results was reported already in ref 20. Indeed, recent results of Intemann et al. which have been obtained in a modified industrial production unit are encouraging.[10]

In an attempt to avoid the TiC formation and carbon incorporation into the film during the deposition, we have used a novel precursor bis[*N*,*N*-bis(*tert*-butyl)-ethylenediamido]titanium (BTET, Figure 1) in expectation that the more stable (*tert*-butyl)ethylenediamido ligands will reduce the contamination. However, no significant improvement was achieved as compared to TMT. The results about the chemisorption of amines at the TiN surface suggest that the contamination is probably due to their decomposition on the growing surface.

Experimental Section

All experiments were performed in an UHV system shown in Figure 2. The substrate, Si(100), was cleaned by Ar$^+$ sputtering and its purity checked by X-ray photoelectron spectroscopy (XPS). All gases were of ≥99.999% purity. The bubbler was kept at 50 °C with argon as carrier gas at 1.05 bar. The typical total pressure in the chamber during the thermal CVD experiment was 0.2 mbar at a carrier gas flow of 25 sccm, the partial pressure of TMT was $\approx 1 \times 10^{-4}$ mbar. In the H-afterglow experiments the ΣH$_x$/TMT ratio was adjusted by first introducing hydrogen into the chamber to set up its desired partial pressure and then adding TMT under

(6) Katz, A.; Feingold, A.; Pearton, S. J.; Nakahara, S.; Ellington, M.; Chakrabarti, U. K.; Geva, M.; Lane, E. *J. Appl. Phys.* **1991**, *70*, 3666.

(7) Katz, A.; Feingold, A.; Nakahara, S.; Pearton, S. J.; Lane, E.; Geva, M.; Stevie, F. A.; Jones, K. *J. Appl. Phys.* **1992**, *71*, 993.

(8) Dubois, L. H.; Zegarski, B. R.; Girolami, G. S. *J. Electrochem. Soc.* **1992**, *139*, 3603.

(9) Sandhu, G. S.; Meikle, S. G.; Doan, T. T. *Appl. Phys. Lett.* **1993**, *62*, 240.

(10) Intemann, A.; Koerner, H.; Koch, F. *J. Electrochem. Soc.* **1993**, *140*, 3215.

(11) Intemann, A. Diploma Work, Technical University Munich, 1991.

(12) Girolami, G. S.; Jensen, J. A.; Gozum, J. E.; Pollina, D. M. *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 429.

(13) Weiller, B. H. *Mater. Res. Soc. Symp. Proc.* **1994**, *335*, 159.

(14) Weiller, B. H.; Partido, B. V. *Chem. Mater.* **1994**, *6*, 260.

(15) Weiller, B. H. *Chem. Mater.* **1995**, *7*, 1609.

(16) Prybyla, J. A.; Chiang, C.-M.; Dubois, L. H. *Mater. Res. Soc. Symp.* **1993**, *282*, 287.

(17) Prybyla, J. A.; Chang, C.-M.; Dubois, L. H. *J. Electrochem. Soc.* **1993**, *140*, 2695.

(18) Truong, C. M.; Chen, P. J.; Corneille, J. S.; Oh, W. S.; Goodman, D. W. *J. Phys. Chem.* **1995**, *99*, 8831.

(19) Merica, R. Ph.D. Thesis, Technical University Munich, in preparation.

(20) Ruhl, G.; Rehmet, R.; Knizova, M.; Veprek, S. *Mater. Res. Soc. Symp. Proc.* **1993**, *309*, 461.

Table 1. Typical Composition of a 300 Å Thick Film Deposited from TMT at 235 °C

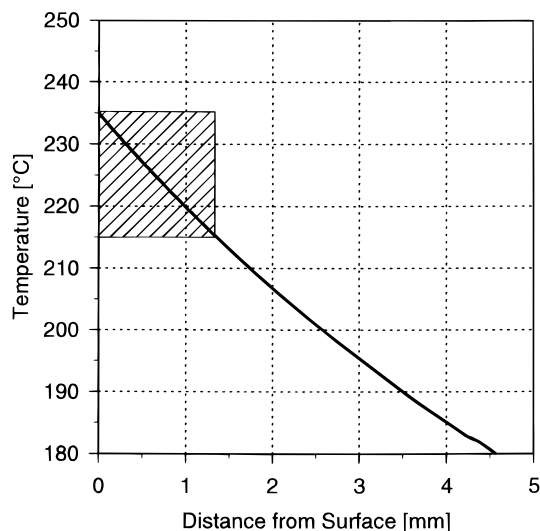|	Ti	N	C	H	O
XPS	1	0.96	1.22	?	≤0.03
RBS/ERD	1	1.25	1.30	1.35	0.75[a]

[a] Oxygen contamination during exposure of the film to air.

its own vapor pressure to give the total pressure of 0.5 mbar. The process gas pressures were measured with a diaphragm gauge. In the BTET experiments, the Ar carrier gas pressure was reduced because of the lower vapor pressure of the precursor (not measured). The Si substrate was mounted on a heatable manipulator which allowed us a fast transfer into the Leybold-Heraeus LHS 10 XPS chamber. The process pump was a 60 m^3/h double-stage rotary pump (RP1, Figure 2) with a molecular sieve trap. The manipulator feed-through was differentially pumped by two-stage rotary pump RP3 (1.5 m^3/h) and turbo pump TP2 (240 L/s), which was also used to evacuate the preparation chamber prior to the transfer of the sample into the XPS chamber. The base pressure in the XPS chamber was typically 5×10^{-10} mbar, and it increased to ≤2 $\times 10^{-8}$ mbar after opening the gate valve to the preparation chamber and introducing the sample. The substrate temperature was calibrated with a Ni/CrNi thermocouple mounted on the substrate surface and checked with an appropriate IR pyrometer. The experiments with thermal decomposition of TMT and the TMT/NH$_3$-system were done without the glow discharge tube. For the hydrogen afterglow experiments we used a conventional direct current (dc) discharge in an U-shaped Pyrex tube (i.d. 39.5 cm, total length 170 cm). This arrangement was chosen to minimize the effect of the electrodes on the H-atom recombination.
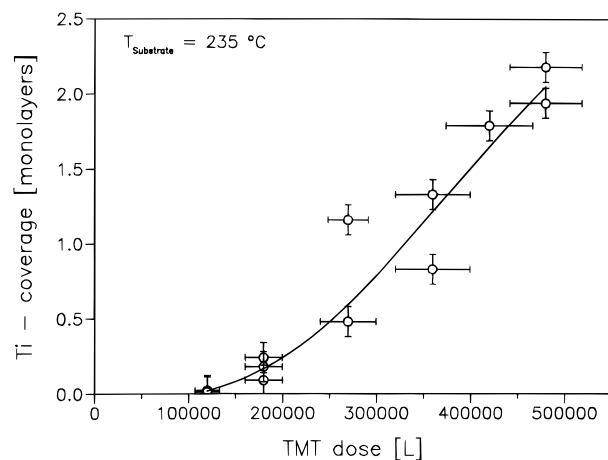
The quantitative analyses of the deposited films were done by in situ XPS with theoretically derived sensitivity factors using cross section data by Scofield.[21] Table 1 shows the composition of a typical film deposited at 235 °C as determined by XPS and compared with Rutherford backscattering and elastic recoil detection (RBS and ERD) data. The RBS and ERD analysis were performed using 3.34 and 2.0 MeV ^{4}He$^+$ ions, respectively. The as-deposited film had a fairly low oxygen content of about 0.6 at. %. During a few days of storage in air prior to the RBS/ERD analysis the oxygen contamination increased to about 13 at. %. Table 1 also shows that the XPS analysis underestimates the content of nitrogen (by a factor of ≈1.3) and carbon (≈1.07). This is due to the fact that a part of the N1s and C1s signal intensities are present in broad inelastic loss peaks that are difficult to quantify. Thus the nitrogen content determined by XPS should be multiplied by a factor of ≈1.3. This correction was done in all reported data. The titanium surface coverage was calculated from the ratio of the Ti 2p$_{3/2}$ and the Si 2p$_{3/2}$ substrate signal.

Results and Discussion

Thermal Deposition from TMT. In a first series of experiments we verified that the deposition reaction starts at a substrate temperature of about 215 °C. The subsequent experiments were done at a substrate temperature of 235 °C in order to be close to the onset of the reaction and thus to minimize the decomposition of the volatile reaction products. Computer simulations (PHOENICS-EARTH 2.0) of the heat distribution in the gas phase under our experimental conditions (p_{total} = 0.2 mbar, flow(Ar) = 25 sccm) show that the zone with a temperature higher than 215 °C does not exceed a distance of 1.3 mm from the substrate surface (Figure 3). Under the same conditions the mean free path of gas molecules is about 0.6 mm. Due to only a few collisions in the "hot" zone the heat transfer from argon

(21) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

Figure 3. Computer simulation data of the gas-phase temperature as a function of the distance from the heated substrate surface (flow(Ar) = 25 sccm, p_{total} = 0.2 mbar). The hatched area indicates the distance within the decomposition temperature of the TMT precursor is exceeded.
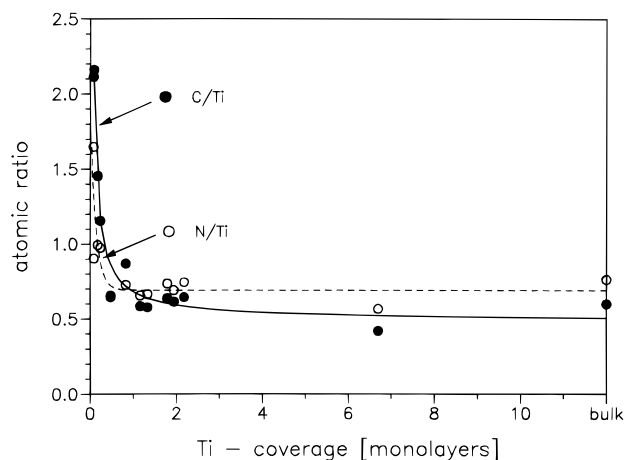

Figure 4. Dependence of the surface coverage normalized to Ti on the exposure to TMT at $p_{TMT} \approx 10^{-4}$ mbar, T_S = 235 °C (dose of 1 Langmuir = 10^{-6} Torr s).
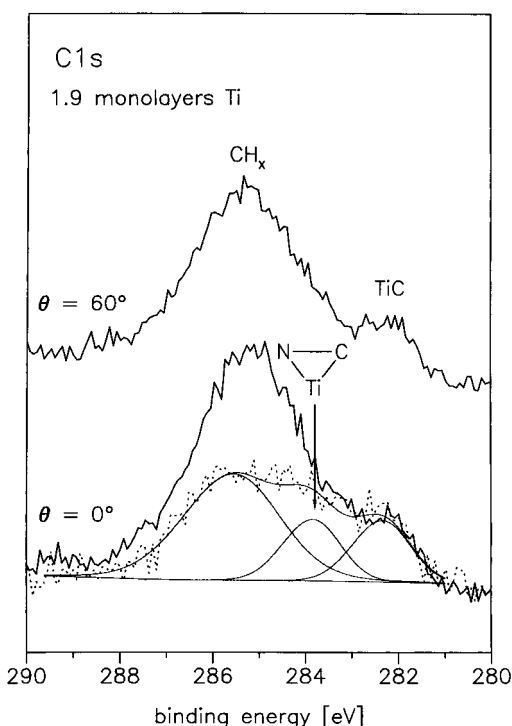
to TMT molecules is very inefficient. Accounting for the relatively low rate constant of 1.1×10^{-16} cm^3 molecules^{-1} s^{-1} reported for the transamination reaction[13,14] and the fact that the thermal decomposition is much slower than the transammination, we conclude in accord with Truong et al.[18] that the decomposition of TMT molecules in the gas phase is very unlikely. At the TMT partial pressure $p_{TMT} \leq 10^{-4}$ mbar, binary gas-phase collisions of two TMT molecules in the near-surface region can also be excluded. Therefore, the results obtained in our study are dominated by reactions at the surface.

Figure 4 shows the dependence of the surface coverage normalized to titanium versus the total exposure to TMT. After an incubation period (which also has been reported by Katz et al.[6] for the reaction in the gas phase) the thickness of the deposited film is proportional to the TMT dose. The dependence of the N/Ti and C/Ti ratio on the titanium coverage (Figure 5) shows that the deposition commences with a stoichiometry of TiNC$_2$ (hydrogen is not detected by XPS). Films thicker than 1 monolayer approach the bulk composition of about TiN$_{0.7}$C$_{0.6}$. The origin of the incubation period is prob-
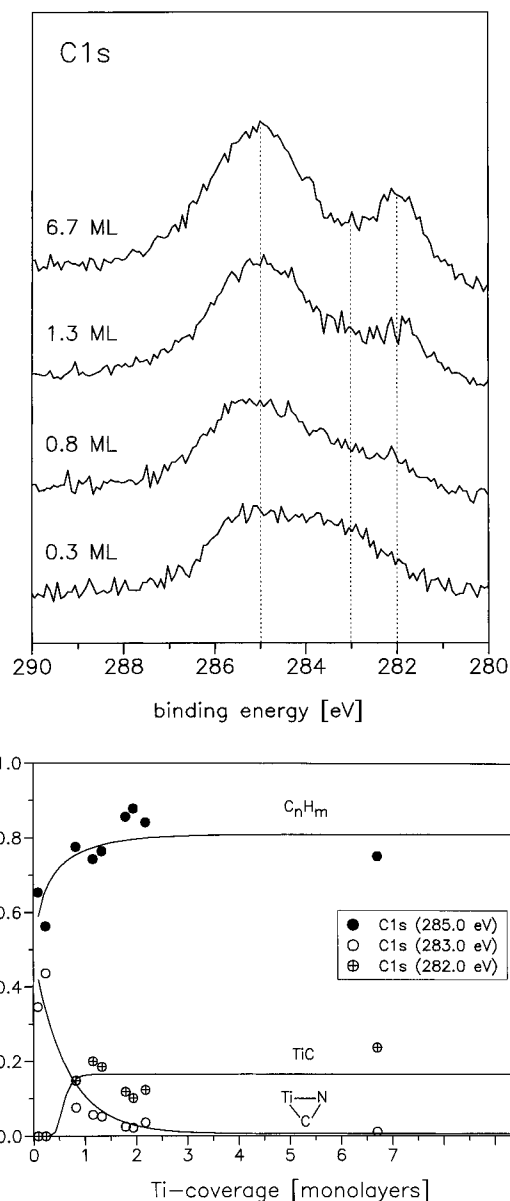
Figure 5. Dependence of the C/Ti and N/Ti ratio in the films on the total coverage normalized to titanium.

Figure 6. Detail spectrum of the C1s signal at a normal (0°) and glancing (60°) takeoff angle. Dotted line: same spectrum after annealing at 275 °C for 10 min under UHV. The deconvolution of the signal into three chemical species is shown as indicated.

Figure 7. (a, top) C 1s spectra at different surface coverages (normalized to the same peak height). (b, bottom) Dependence of the fractions of the different carbon species in the C1s signal on the coverage normalized to Ti.

ably the deposition of a NC$_2$H$_x$-rich layer on the originally clean Si surface, which slows the decomposition of TMT molecules.
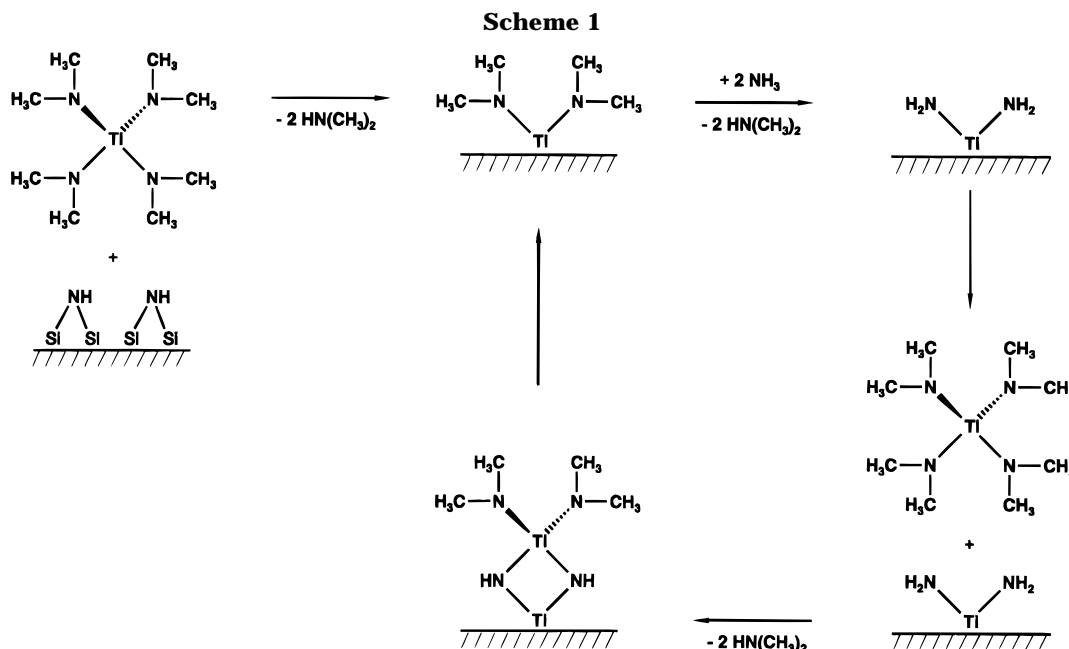
Detailed spectra show that the C1s signal consists of three components at binding energies of 282.0, 283.0, and 285.0 eV (see Figures 6 and 7a). The signal at 282.0 eV corresponds to the carbidic carbon in TiC.[22] We propose that the second component at 283.0 eV can be explained by titanium-bound carbon shifted to a higher binding energy by simultaneously binding to more electronegative nitrogen. Interactions of the deposited carbon with the silicon substrate are excluded because of the identical Si2p signal shapes before and after the deposition. Thus this species can be attributed to the

carbon atom in a Ti−C−N three-membered ring which has been found by Dubois et al. by FTIR spectroscopy.[8] The signal at 285.0 eV can be assigned either to aliphatic hydrocarbons or to graphitic carbon. Annealing of a 1.9 monolayers thick film under UHV conditions at a temperature slightly higher ($T_S = 275$ °C) than the deposition ($T_S = 235$ °C) results in the decrease of the C1s signal at 285.0 eV (Figure 6, dotted line). This evidences that this component consists mainly of volatile hydrocarbons trapped in the film. Mass spectroscopic measurements showed the desorption of C$_n$H$_m$ with $n = 1, 2, 3$. As the N/Ti ratio remains unchanged during the anneal, we conclude that no nitrogen-containing species desorb. Films prepared at the same temperature but a 20 times higher deposition rate ($p_{total} = 1$ mbar, bubbler temperature 70 °C) showed a significantly higher hydrocarbon content. This effect is either due to a hindered desorption of the hydrocarbon products during the deposition, or to a decomposition of the volatile carbon-containing reaction product on the me-

(22) Ramqvist, L.; Hamrin, K.; Johansson, G.; Fahlmann, A.; Nordling, C. *J. Phys. Chem. Solids* **1969**, *30*, 1835.

Scheme 1

- 2 HN(CH₃)₂

+ 2 NH₃
- 2 HN(CH₃)₂

- 2 HN(CH₃)₂

tallic surface of the growing film. Indeed, we could show that amines but neither ethane nor ethylene adsorb and decompose on the TiN surface (see below).

The plot of the fractions of the three components of the total C1s signal versus the film thickness (Figure 7b) shows that the initially adsorbed species contain the Ti–C–N ring and C_nH_m in the (extrapolated) ratio of about 1:1. The corresponding N1s spectra show the occurrence of a small feature at a binding energy of 398.2 eV, which is shifted by 1.1 eV to higher binding energies with respect to the signal from TiN at 397.1 eV.[23] Because of the absence of a corresponding C1s peak at 285.7 eV for methylamines,[24] directly organic bonded nitrogen can be excluded. Thus this feature can also be assigned to the proposed titanacycle. At a thickness of 1 monolayer the Ti–C–N ring nearly disappears and the formation of carbide starts leading to a bulk material consisting of TiN_x, TiC_y, and C_nH_m (TiN_x:$TiC_y \approx 6$:1). The N1s signal at 398.2 eV also disappears at the same film thickness. The disappearance rate of this signal cannot be directly correlated to the C1s feature at 283.0 eV because of its location in the high-energy satellite region of the TiN signal leading to unreliable curve fits. The takeoff angle dependence (Figure 6) of the C1s signal shows that at a titanium coverage of 1.9 monolayers the carbidic carbon is bonded predominantly to the topmost layer. This means that the interface layer at the substrate is hydrocarbon-rich, which increases the electrical contact resistance.

On the basis of these results, we propose the following extension of the established mechanism for the thermal decomposition of TMT at the silicon surface: After the adsorption of a TMT molecule on the hot substrate, a N–Ti–C cyclic intermediate is formed by the elimination of dimethylamine. This reaction step has already been verified by Dubois et al.[8] A subsequent reaction leads to a species with the required stoichiometry of $TiNC_2$. According to the detailed C1s spectra, this product consists of titanacycles and aliphatic hydrocarbons in the ratio 1:1. Another TMT molecule from the gas phase reacts with the titanacycle compound on the surface leading to TiN in the second monolayer. The formation of either TiN or TiC is determined by the kind of bond cleaved in the N–Ti–C ring in the subsequent step. The comparison of the bond strengths (TiN 476 kJ/mol, TiC 423 kJ/mol[25]) shows the preference of TiN formation.
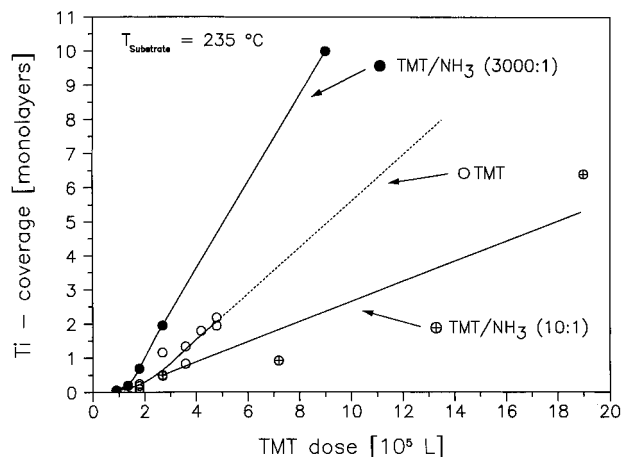
The crucial role of the titanacycle intermediate for the formation of titanium carbide is supported by results of Fix et al.,[3] together with our own results with BTET as precursor discussed later in this paper. Hence the formation of a carbidic bond is inherent to the thermolysis of this organometallic CVD precursor in the initial as well as the later stage of growth. On the basis of their in situ infrared absorption spectra during the thermolysis of TMT on titanium and tantalum surfaces, Truong et al.[18] suggested another mechanism in which the dimethylamine elimination leads to the formation of an adsorbed fragment which contains a group with a C=N double bond (see mechanism A in Figure 4[18]). Our results suggest that this mechanism may be dominant in the later stages of the film growth whereas the metallacycle formation (Scheme 1 in this work and mechanism B in Figure 4 of the paper by Truong et al.[18]) dominates during the formation of the first monolayer at the silicon surface (see Figure 7). The nonvanishing amount of the carbidic carbon (Figure 7) during the later stages of the film growth is a strong indication that the metallacycle formation remains an important (maybe even a dominant) parallel reaction of the TMT thermolysis at the surface.

Deposition from TMT and Ammonia. A series of experiments were done to decrease the carbon content of the films, in particular at the substrate–film interface. The depositions were performed under the same conditions as above but with the silicon substrate pretreated with ammonia at $T_S = 235\ °C$. This resulted

(23) Wu, H. Z.; Chou, T. C.; Mishra, A.; Anderson, D. R.; Lampert, J. K.; Gujrathi, S. C. *Thin Solid Films* **1990**, *191*, 55.

(24) Gelius, U.; Heden, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70.

(25) Kerr, J. A. In *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press: Boca Raton, 1990; p F-197.
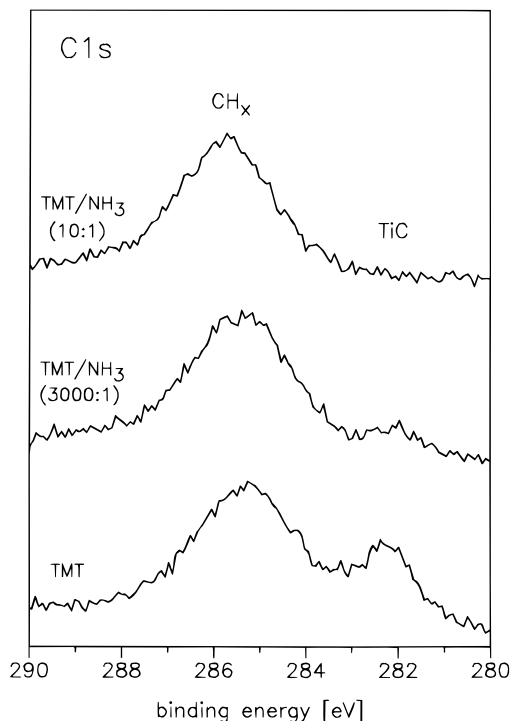
Figure 8. Dependence of the surface coverage normalized to Ti on the exposure with TMT at different TMT/NH$_3$ ratios.
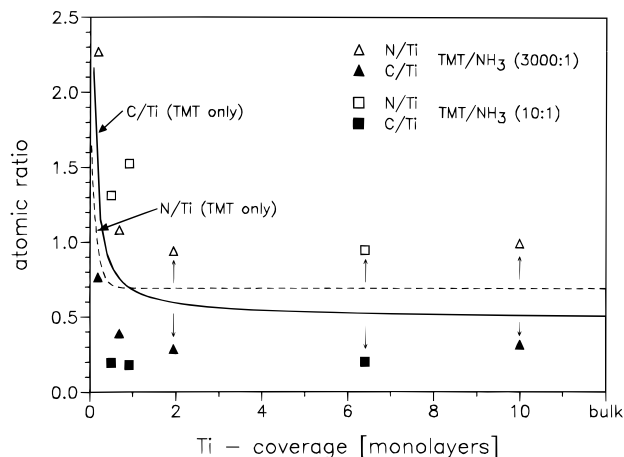
in a nitrogen coverage of about 0.2 monolayer bound as silicon amide and imide in accordance with the data of Larsson and Flodström.[26] Simultaneously, the walls of the chamber (at room temperature) were saturated with adsorbed ammonia which, after pumping down for a few hours, sets up an almost constant pressure of $p(NH_3) \approx 5 \times 10^{-8}$ mbar in the chamber. This results in a TMT/NH$_3$ ratio of 3000:1 in the gas phase and, because a smaller thermal velocity of TMT as compared with NH$_3$, a somewhat smaller ratio in the flux of the molecules to the surface. The enhanced deposition rate for thicker films than 1 monolayer (Figure 8) shows that the reaction occurs at the surface, where at the given deposition rate of 8 monolayers of Ti(N,C) per hour, a fresh TiN surface sees the dose of $\approx$20 langmuirs of NH$_3$. The presence of a small amount of carbidic carbon as seen in Figure 9 shows that the thermolytic reaction still proceeds simultaneously although with a reduced rate.

From these data the film growth reaction of TMT with NH$_3$ can be explained by a polymeric transamination, such as, e.g., Scheme 1. Of course, the individual steps of this complex reaction may somewhat differ in detail, such as a reaction between TMT and NH$_x$ both in an adsorbed state at the surface as suggested for Ti and W surfaces by Truong et al.[18] or a stepwise elimination of HN(CH$_3$)$_2$ in the last step of reaction 3. The available experimental techniques, in particular the lack of possibility of measuring the amount of hydrogen and its nature at the surface, allow one to suggest a plausible mechanism but not to confirm it definitively.

To verify if such a mechanism is also valid for the gas-phase reaction, the TMT/NH$_3$ ratio was changed to a lower but still far understoichiometric value of 10:1. The shift of the reaction to the gas phase can be observed by the lower deposition rate at the substrate (Figure 8) because a gas-phase depletion due to the deposition at the walls of the reaction chamber. After the substrate pretreatment with NH$_3$ as described above, the NH$_3$ flow was kept constant and TMT was added. The total pressure was again 0.2 mbar and the TMT/NH$_3$ ratio was 10:1. The absence of carbidic bonded carbon (Figure 9) shows, that the reaction now proceeds completely via the polymeric transamination path. This interpretation is consistent with results by

(26) Larsson, C. U. S.; Flodström, A. S. *Surf. Sci.* **1991**, *241*, 353.

Figure 9. Detail spectrum of the C1s signal at different TMT/NH$_3$ ratios (normalized to the same peak height).
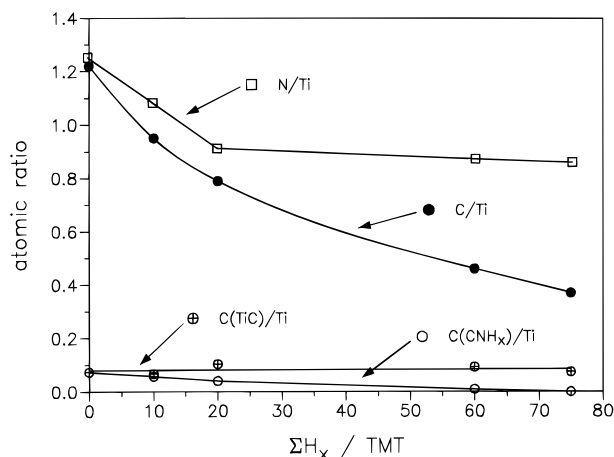

Figure 10. Dependence of the C/Ti and N/Ti ratio in the films on the coverage normalized to Ti for two different TMT/NH$_3$ ratios. The solid and broken lines show the corresponding data from thermal TMT decomposition. The arrows indicate the increase of nitrogen and decrease of carbon content in the films deposited with NH$_3$ and TMT as compared with TMT only.

Prybyla et al.[16,17] and also with the more recent paper of Truong et al.[18]

Figure 10 shows that the pretreatment of the substrate with ammonia followed by the deposition at TMT/NH$_3 \approx$ 3000:1 already results in a strong decrease of the carbon contamination at the interface. Evidently, the chemisorbed NH$_x$ species from the pretreatment are sufficient to remove the dimethylamino ligands as gaseous amines avoiding the formation of the metalla-cycle. The carbon content further decreases to about 6 at. %, if the TMT/NH$_3$ ratio is decreased to 10:1. A further increase of the ammonia partial pressure minimizes the carbon content to 1–3 at. %.[4,10,18]

A disadvantage of the TMT/NH$_3$ system is the fact that a significant part of the incorporated nitrogen is bonded to hydrogen, which makes it very reactive.

Figure 11. Dependence of the carbon and nitrogen content on the total hydrogen/TMT ratio.
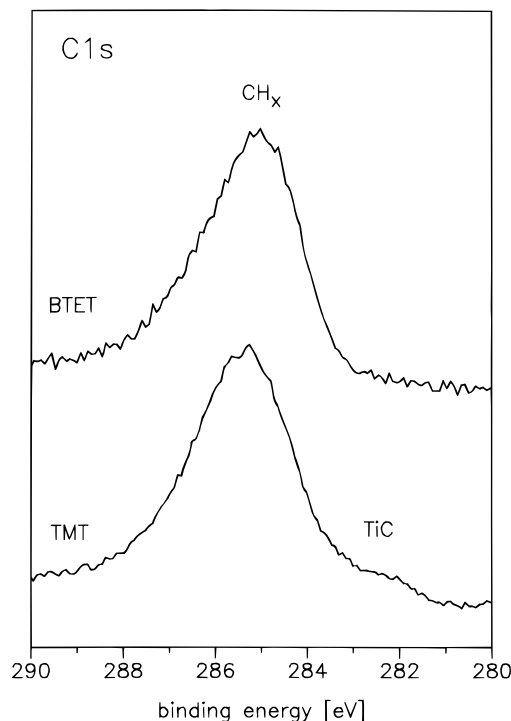
Detailed Ti2p spectra show that the films react with the residual oxygen in the chamber (total pressure of O_2, H_2O, and their fragments less than 10^{-9} mbar) forming oxides within a few hours, whereas thermally deposited films from TMT alone are stable toward oxidation for a few days.

Deposition from TMT and H Atoms. We have shown earlier that atomic hydrogen as coreactant provides an alternative reaction system to minimize hydrocarbon contaminations.[20] Because of its small size and high reactivity, atomic hydrogen can stabilize the hydrocarbon and amino leaving groups. Figure 11 shows the decrease of the total carbon content to ≤10 at. % (H content estimated as 1) at $\sum H_x$/TMT ≥75, whereas the carbidic carbon-to-titanium ratio stays constant at 0.1. This shows that the H radicals do not affect the thermolysis reaction. The nitrogen content decreases with increasing hydrogen concentration until it reaches a constant value of about 0.9 (calibrated with RBS) at $\sum H_x$/TMT ≥20. Simultaneously the signal of a nitrogen-bound carbon species (binding energy 287.0 eV) decreases. This stoichiometry suggests that the deposited material consists of a solid solution of TiN and TiC with the composition $TiN_{0.9}C_{0.1}$ containing hydrocarbons in defects and grain boundaries.

The limited pumping speed of the vacuum pump did not allow us to reach higher $\sum H_x$/TMT ratios than 75, but we expect that with higher H concentrations the carbon content should be reduced to ≈3 at. % of carbidic carbon. Intemann et al.[10] who used a microwave afterglow source and higher pressure and gas flow rate, could decrease the carbon content also to about 10 at. %. Such films show a good diffusion barrier performance up to 550 °C and a very good step coverage of almost 100% (aspect ratio of 1:1).[10]

Annealing experiments on thick films were done at an annealing temperature of 385 °C in 0.2 mbar of NH_3 atmosphere to check if the hydrocarbon impurities can be removed and the nitrogen content increased in this way. XPS sputtering depth profiles showed that under these conditions the hydrocarbons desorb only from the topmost monolayer and the nitrogen content stays constant.

Deposition from BTET and H Atoms. Fix et al. suggested preventing the carbide formation during thermal decomposition by blocking the metallacycle formation by inserting the ligand β-carbon in an ali-

Figure 12. Detail spectra of the C1s signal of films deposited from TMT and BTET (normalized to the same peak height).
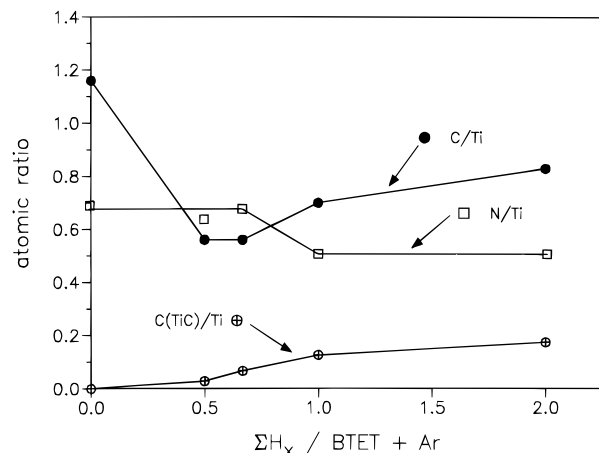
Table 2. N and C Content of Films Prepared from Precursors with Different Bond Types of the β-Carbon (Data for Ti(NC$_4$H$_8$)$_4$ Taken from Ref 3)

precursor	$T_{substrate}$ (°C)	N/Ti	C/Ti
$Ti(NMe_2)_4$	235	1.25	1.3
$Ti(NC_4H_8)_4$	400	1.2	3.3
$Ti(N_2C_2H_4{}^tBu_2)_2$	375	0.72	1.16

phatic heterocycle. The films deposited from the corresponding precursors (e.g., tetrakis(pyrrolidino)titanium) contained no carbide but a large amount of hydrocarbons.[3] We chose bis[N,N'-bis(tert-butyl)ethylenediamido]titanium (BTET)[27] because of its minimized ring size and *tert*-butyl groups as stabilizing ligands, which are supposed to give stable leaving amino groups.

The depositions were performed at a substrate temperature of 375 °C and a pressure of 0.5 mbar. The comparison of the film compositions deposited from TMT, Ti(NC$_4$H$_8$)$_4$,[3] and BTET suggest that the *tert*-butyl groups in BTET indeed probably leave as relatively stable radicals leading to a carbon content even lower than in films deposited from TMT. This interpretation is consistent with the results of Fix et al. on Ti-[N(CH$_3$)$_2$]$_3$($^tC_4H_9$).[3] As shown in Figure 12 also the carbidic carbon component disappears as intended. The decrease of the nitrogen content suggests that the ethylenediamino ligands are partly leaving without cleavage. Experiments with BTET and H-afterglow were done to further decrease the hydrocarbon contamination in the films without carbide formation. The results in Figure 13 show the presence of two different regimes with increasing hydrogen afterglow concentration $\sum H_x$. For a low hydrogen concentration ($\sum H_x$/BTET + Ar ≤ 0.7) the total carbon concentration decreases to a minimum of ≈18 at. %. This can be explained by the saturation of the leaving groups similar to the deposition

(27) Denk, M. Ph.D. Thesis, Technical University Munich, 1992.

Figure 13. Dependence of the N/Ti, total C/Ti, and C(TiC)/Ti ratios on the total hydrogen/BTET + Ar ratio. Because of the not measured vapor pressure of BTET, the sum of BTET and argon partial pressure is given.
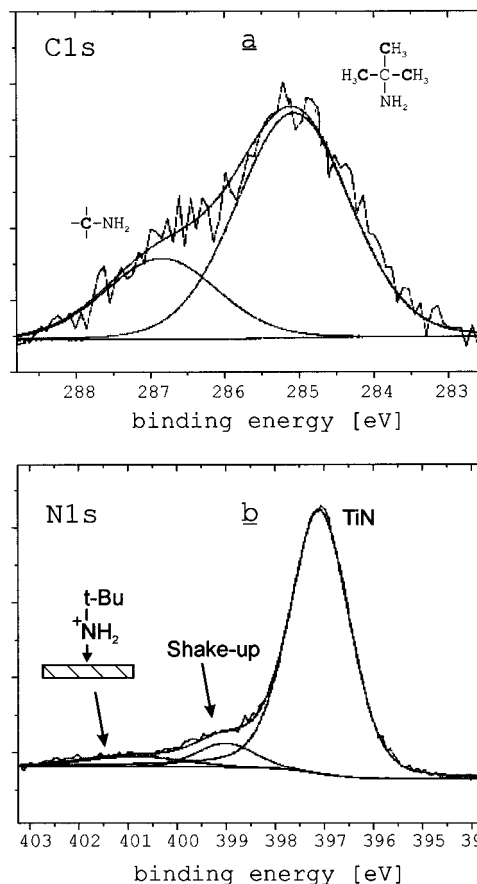
from TMT. Simultaneously an increasing carbide formation occurs probably caused by the breaking of C−C bonds in the ethylene bridges. The constant nitrogen concentration obviously shows that the Ti−N bonds are not attacked. In the second regime at ΣH_x/BTET + Ar ≥ 0.7, the nitrogen concentration in the films decreases. We suggest that here the H atom concentration is obviously high enough to cleave the Ti−N bonds leaving partially unsaturated Ti centers. These centers are supposed to react with hydrocarbons leading to a further increase in carbide formation.

Our results show that the BTET precursor yields no major improvement compared with TMT neither in the thermal reaction nor in the H-afterglow reaction. The nitrogen concentration is understoichiometric by far and the carbon contamination cannot be decreased to the low values of the TMT/H-afterglow deposited films. Similar results were obtained with other related spirocyclic precursors, such as *N,N*-bis[di-*tert*-butyl-1,4-diazadiene-1,3]titanium(IV) and bis[*N,N*-bis(trimethylsilyl)ethylenediamido]titanium(IV).[28]

Possible Contribution of the Secondary Reactions to the Carbon Contamination of the Films. The formation of the metallacycle by reaction 1 is a plausible origin of the contamination of the TiN by the carbidic carbon. However, the mechanism of the incorporation of the "organic" carbon (C1s signal at 285 eV), which dominates the contamination, is not unambiguously explained by any of the reaction mechanisms suggested in this paper or elsewhere (e.g., ref 18). One may only speculate if it occurs during the TMT decomposition due to occurrence of other reactions than the elimination of amines which were not considered so far or if the leaving reaction products amines (or hydrocarbons) could chemisorb at the surface of the growing TiN film. For this reason we have compared the adsorption of ethane, ethylene and *tert*-butylamine on a clean TiN surface. *tert*-Butylamine was chosen because of its expected large stability against dissociative chemisorption (as compared, e.g., with HN(CH$_3$)$_2$) and the resulting possibility of an easy interpretation of the adsorbate state.

The TiN films were prepared by plasma-induced CVD from TiCl$_4$ and ammonia with a large excess of H$_2$ at a

Figure 14. C1s (a) and N1s (b) XPS signals from a monolayer of *tert*-butylamine adsorbed at TiN (see text).

substrate temperature of 450 °C, which yields stoichiometric TiN films with a low chlorine content of few tenths of an at. %.[29,30] To avoid contamination of the surface and the loss of nitrogen by sputter cleaning,[19] the films were deposited on an Fe substrate which was mounted on the manipulator (see Figure 2), characterized in situ by XPS and immediately afterward exposed to the chosen gas. A series of exposures was done at a TiN temperature of 22, 250, and 450 °C, a gas pressure chosen between 10^{-5} and 10^{-3} mbar and exposition period up to 15 min. No carbon adsorption was found (sensitivity better than 0.05 monolayer) for ethane and ethylene even for the largest exposure corresponding to about 10^5 langmuirs and the temperature between 22 and 450 °C. However, *tert*-butylamine adsorbs readily at the TiN surface, forming a bond between the nitrogen atom and the TiN surface. This is illustrated by the C1s spectra shown in Figure 14a, which show two components with an intensity ratio of 3:1 and a binding energy of 285 and 287 eV, respectively. The intensity ratio exactly corresponds to the three C atoms in the methyl groups and one bonded to nitrogen (see Figure 14a). The binding energy of the latter is shifted to higher value due to the effect of the more electronegative nitrogen,[31] whereas the binding energy of the carbon atoms in the methyl groups corresponds to 285 eV. The N1s spectrum (Figure 14b) shows the typical signal from TiN at 397.1 eV with a shakeup satellite at about 399

(28) Prokop, J. Ph.D. Thesis, Technical University Munich, 1995.

(29) Patscheider, J.; Shizhi, Li; Veprek, S. *Plasma Chem. Plasma Processing,* in press.

(30) Veprek, S.; Reiprich, S. *Thin Solid Films* **1995**, *268*, 64.

(31) *Handbook of X-ray Photoelectron Spectroscopy*; Perkin Elmer Corp., 1978.

eV[32] and a weak signal at about 401 eV which is attributed to the nitrogen in *tert*-butylamine adsorbed at the TiN surface, in agreement with literature data on various amino and related compounds.[31,33−34] It is not possible to prove if the nitrogen is bonded to the surface via the electron lone pair being still bonded to the two hydrogen atoms or if the nitrogen−hydrogen bonds were broken. However, the data clearly show that the electron lone pair plays at least the role of the initial coordination center, thus enhancing the adsorption probability as compared with ethane and ethylene. (A similar effect has been found recently for a cyclic germylene.[35]) Therefore, even if the dimethylamine is formed via the β-elimination during thermal decomposition of TMT as discussed above, it will easily chemisorb and decompose at the surface of the growing film. The effect of hydrogen afterglow is now also understood: The atomic hydrogen reacts with the methyl groups (or any other CH_n(ads) ones) forming methane which can leave the reactor.

Conclusions

The results show that even at very low partial pressures of the precursor, where the reactions in the gas phase are suppressed, the thermal CVD from tetrakis(dimethylamido)titanium yields $TiN_xC_yH_z$ films with a high hydrocarbon and TiC content. Moreover,

in the initial stages of the deposition on silicon a hydrocarbon-rich interface layer is formed. Similar results were reported recently also for the deposition on Ti, W, and Ta surfaces.[18] Ammonia as coreactant avoids the formation of this interlayer and reduces the carbon content of the bulk films. However, besides the poor step coverage due to the fast gas-phase reaction, a relatively high content of reactive NH_x groups results in the fast incorporation of oxygen upon exposure of the films to air.

The hydrocarbon contamination can be reduced and the quality of the films significantly improved by using the deposition from TMT with hydrogen plasma afterglow. The atomic hydrogen reacts with the ligand groups forming volatile hydrocarbons. The thermolytic reaction pathway remains essentially unaffected. This is probably responsible for good step coverage of structured wafers as found by Intemann et al.[11] Postannealing of the films in ammonia does not change the film composition. Depositions from bis[*N,N*-di-*tert*-butyl-ethylenediamido]titanium (BTET) with hydrogen afterglow does not lead to titanium carbide-free films with a low hydrocarbon content. Finally it was shown that chemisorption of amines at the TiN surface is a possible contribution to the high carbon contamination. These results lead to the conclusion that the TMT with hydrogen afterglow is promising OMCVD system for low carbon TiN with a good step coverage.

(32) Wu, N. Z.; Chou, T. C.; Mishra, A.; Anderson, D. R.; Lampert, J. K.; Gujrathi, C. *Thin Solid Films* **1990**, *191*, 55.

(33) Remy, M. J.; Genet, M. J.; Lardionis, P. F.; Notteé, P. P.; Poncelet, G. *Surf. Interface Anal.* **1994**, *21*, 643.

(34) Borade, R. B.; Kaliaguine, A. S. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3949.

(35) Veprek, S.; Prokop, J.; Glatz, F.; Merica, R.; Klingan, F. R.; Herrmann, F. R. *Chem. Mater.* **1996**, *8*, 825.